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Summary of Evidence for the Possible Natural Formation of Dioxins in Mined Clay Products

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Introduction

Ball clay was the source of elevated dioxin levels in a variety of animal food products in the United States ¹. The ball clay had been used as an anti-caking agent in the soy component of animal feeds. Its use in animal feeds has been discontinued. In a joint effort between the USEPA and the FDA to evaluate the distribution of dioxins in mined products used in animal feeds, raw ball clay, processed clay and a variety of other mined products have been analyzed for the presence of dioxins and furans (CDD/CDFs) ². The isomer distribution and the congener profile in the ball clay were established ³ and are distinctive with characteristic features unique to this particular type of clay. These features have also been found to be exhibited by dioxins found in clays in other locations in the United States and in Germany ⁴. These characteristics are distinguishable from and do not match those from other known sources and provides evidence which supports a hypothesis attributing their presence to natural processes.

Material and Methods

Eight raw ball clay samples were obtained from an open mining pit at a depth of 50-60 feet by boring horizontally into the wall adjacent to an excavated area to obtain clay not previously exposed to the atmosphere. Four processed ball clay samples were obtained as sub-samples from larger bulk quantities commercially available. An additional sixteen mined products used in animal feeds were obtained by the FDA at a variety of commercial processing locations in the United States. Details of the analytical procedure are described elsewhere ³ and are based on a modified version of EPA's Method 1613.

Results and Discussion.

The average concentration of the 2,3,7,8-Cl substituted dioxins from the analyses of the raw and processed ball clay are provided in Table 1 together with the average concentrations of the total homologue groups. OCDD was the congener at the highest concentration in all of the samples followed by either HpCDD and, surprisingly, in two of the samples by the 1,2,3,7,8,9-HxCDD. The most toxic tetra and penta congeners are present at unusually high concentrations in all of the

samples with average concentrations of 711 and 508 ppt, respectively. For the processed ball clay, OCDD was again present at the highest concentration with its absolute and relative concentration being much higher than in the raw clay with an average concentration exceeding 200 ppb. The HpCDD was the next highest in concentration followed in all cases by the 1,2,3,7,8,9-HxCDD. Although the PeCDD concentration was approximately equal in the raw clay and the processed clay with average concentrations of 500 and 430 ppt respectively, there was a dramatic reduction in the TCDD concentration in processed clay. The average concentration of the TCDD in the raw clay was 700 ppt but dropped to approximately 50 ppt in the processed clay. Another interesting feature in the ball clay is the presence of 1,2,3,7,8,9-HxCDD at higher concentrations than the other 2,3,7,8 HxCDD isomers.

As is evident from the homologue totals, the furan concentrations, while detectable, are dramatically lower than the dioxins in each homologue group and the relative concentrations of each individual to the total is markedly different between the raw and processed clay. The 2,3,7,8-Cl substituted furans were also not detected at comparable detection limits (LOD = 1ppt) or were present at 2-3 orders of magnitude lower.

Six of the other sixteen mined products were relatively free from detectable levels of CDD/CDFs including OCDD. These included all five sodium bentonites from the New England states, the bentonites and sodium bentonite from Wyoming and the attapulgite from Florida. For the other samples, OCDD was found at the highest concentration followed without exception by the HpCDD and then the 1,2,3,7,8,9-HxCDD which, as in all the mined products including the ball clay, is present at higher concentrations than the other two toxic hexa isomers. This is unusual since, in most cases, the 1,2,3,6,7,8 is the dominant congener among the toxic hexa isomers, especially in biological media.(5). The I-TEQs for the mined products are: lime 0.43, Al-Ca-silicate 0.52, bulk clay 0.97, montmorillonite 0.84-4.81, ground clay 9.75 and bentonite 3.93 and 22.4 ppt.

The isomer distribution and congener profile for the ball clay has also been determined and displays some interesting and apparently unique features that provide the basis for comparisons to these characteristics from known dioxin sources. In addition to the high concentrations of 2,3,7,8-TCDD and the predominance of the 1,2,4,7,8,9-HxCDD and the absence of furans at comparable concentrations, the tetra isomer distribution also appears to be a distinctive feature of the ball clay.

As is evident from Figure 1, the tetra profile is dominated by the 2,3,7,8-, 1,2,7,8-, 1,2,6,7- and the 1,2,8,9- isomers. This is in marked contrast to the profile of a "typical" air sample in which these isomers are minor components and the profile is dominated by the 1,3,6,8- 1,3,7,9-, 1,3,6,9-, and the 1,2,4,9-/1,2,4,8- (unresolved) congener pair. In air samples, furans are predominant components, reflecting combustion sources, while there is a marked absence of these components in ball clay. This pronounced dissimilarity between the tetra isomer dioxin distribution in the ball clay and air strongly argues for a source other than combustion to account for dioxins in the clay. Even if it is assumed that the clays have been acting as a sink for the accumulation of air deposited CDD/CDFs over extended periods of time, the absence of furans and the unusual tetra dioxin profile remain unexplained.

Cleverly et al ⁶ compiled congener profiles that are typical of wide variety of known anthropogenic sources of dioxin in the U.S. and their analyses was used as a basis for comparison

to the profile of the ball clay. None of the profiles examined match the characteristics of the ball clay. For example, the congener profile of technical grade pentachlorophenol is clearly dominated by OCDD and HpCDD as in the ball clay. However, PCP contains only trace levels of 2,3,7,8-TCDD and the 1,2,3,4,6,7,8-HpCDF and OCDF constitute roughly 15 % of typical formulations.

The natural origin and production of various dioxin congeners by natural processes has been suggested by a number of investigators. Lamparski et al ⁷ reported that hexa-, hepta- and octa-dioxin congeners in sewage sludge sealed in an ampule from 1933 matched the pattern found in sewage sludge from the 1980s. Since the 1933 sample predated the commercial production of PCP (a likely source for these congeners), a natural chlorination process was proposed to account for their presence. Similarly, Svenson et al ⁸ Oberg et al ⁹, Rappe et al ¹⁰ and Silk et al ¹¹ all report enzyme mediated dioxin formation from chlorophenols.

The presence and natural production of a wide variety of halogenated organics including as assortment of chlorinated phenols by ancient species of blue green alga, fungi, and numerous other pre-historic organisms is described in detail by Gribble ¹². More recently, Hoektra et al ¹³ has demonstrated the natural formation of chlorinated phenols and chlorinated CDD/CDFs in the soil of a Douglas fir forest and has proposed a mechanism responsible for their formation. The accumulation of these naturally formed chlorinated materials in the clay deposits over the eons could conceivably have supplied the precursor material for the formation of the dioxins in the clays. The production of dioxins from chlorophenols is well documented and the examples sited herein invites speculation that the dioxins in the clays could have possibly been derived from naturally produced chlorophenols by a yet explained mechanism.

Other ball clay samples originating from mines in Kentucky also were found to contain dioxins at comparable concentrations to those found in the mine from Mississippi and share the same features noted for the isomer distributions. Recently, dioxins have been discovered in kaolinitic clay in Germany and they too display the same characteristic features of the ball clay from the United States ³. No anthropogenic source was suspected and it was speculated that the dioxins were a result of some geologic process. These recent findings of elevated dioxin levels in clay deposits millions of years old in disparate regions of the U.S. with distinct unprecedented isomer patterns that reportedly match those originating from ancient deposits in Germany argues for some natural geologic mechanism to account for their origin ¹⁴. To date, no definitive experimental evidence has been brought forward to account for the presence of the dioxins in the clay from known anthropogenic sources or to account for their synthesis under natural conditions.

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Table 1. Average Concentration of 2,3,7,8-Cl Substituted PCDDs and Total CDDs/CDFs in Ball Clay [ppt, d.w.]

Congener	Raw	Processed	Total	Raw	Processed
2,3,7,8-TCDD	711	48	TCDD	3729	2425
1,2,3,7,8-PeCDD	508	432	TCDF	6	11
1,2,3,4,7,8-HxCDD	131	593	PeCDD	4798	7378
1,2,3,6,7,8-HxCDD	456	738	PeCDF	2	1
1,2,3,7,8,9-HxCDD	2093	2028	HxCDD	6609	21034
1,2,3,4,6,7,8-HpCDD	2383	14041	HxCDF	6	12
OCDD	20640	205663	HpCDD	6194	30420
			HpCDF	9	55
Total TEQ	1513	977	OCDD	20640	211244
			OCDF	11	23

Figure 1. Tetrachloro-dibenzo-p-dioxin isomer distributions of Ball Clay and Air

